



Hydrogen production from bio-ethanol steam reforming reaction in a Pd/PSS membrane reactor

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ABSTRACT

The aim of this work is to explore the potentiality of a porous stainless steel (PSS) supported Pd-based membrane reactor (MR) for hydrogen production via bio-ethanol steam reforming reaction (BESR). Bio-ethanol may be produced from fermentation of cheese by-product waste, which contains major impurities like acetic acid and glycerol. In this work, a simulated bio-ethanol mixture is utilized and contains besides ethanol and water also acetic acid and glycerol with 1:13:0.18:0.04 molar ratio, directly supplied to the MR. In the overall experimental campaign, BESR reaction is performed at 400 °C and in a reaction pressure range of 8–12 bar (abs.) using both Ni/ZrO₂ and Co/Al₂O₃ commercial catalysts, packed in the annulus of the membrane reactor. The present study illustrates the influence of the reaction pressure and gas-hour-space-velocity on the MR performances in terms of bio-ethanol conversion, hydrogen recovery factor (HRF), hydrogen permeate purity (HPP) and yield of hydrogen. Furthermore, the effect of the by-products such as acetic acid and glycerol on the MR performances is investigated. In Pd/PSS MR, the best result of this work is obtained at 12 bar and 800 h⁻¹ as GHSV and using the Co-based catalyst with around 94% of bio-ethanol conversion, 40% of hydrogen yield and HRF ~40% with a HPP of 95%.

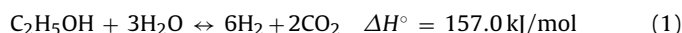
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1. Introduction

Most of the hydrogen produced today comes from catalytic steam reforming (SR) of natural gas [1]. Indeed, SR is a mature technology for hydrogen production, which is not only used in chemicals, fertilizers production and petroleum refineries but also, in high purity concentration, as a clean fuel to supply PEM fuel cells. However, owing to the environmental pollution caused by using derived of fossil fuels, the scientific community is involved on studying the use of alternative and renewable materials having minimal or no impact on the environment [2]. In particular,

biomass-derived feedstocks, especially 2nd generation bio-fuels from agro, industrial and food wastes (potato, cheese waste by-product, etc.), may represent alternative raw materials for hydrogen production [3]. For example, bio-fuels like ethanol, glycerol and butanol can be easily reformed to hydrogen and carbon dioxide [3,4].

However, reformed gases with high hydrogen concentration and a CO content lower than 10 ppm are needed for supplying PEM fuel cells used in both transport and stationary applications [5]. Therefore, BESR reaction (1) (main reaction) for hydrogen production is widely studied due to its availability, low feed toxicity and high H/C ratio [5].



Using hydrogen from bio-ethanol is much more efficient than bio-ethanol used directly in internal combustion engine (ICE) and/or blended with gasoline. In fact, the fuel up-grade of ethanol requires various purification steps prior to be blended with gasoline or supplied to an ICE. In details, the expensive distillation as a crucial step of ethanol purification makes high capital and operating costs for water free ethanol production. On the contrary,

Abbreviations: PSS, porous stainless steel; MR, membrane reactor; BESR, bio-ethanol steam reforming; HRF, hydrogen recovery factor; HPP, hydrogen permeate purity; SR, steam reforming; PEM, polymer electrolyte membrane; ICE, internal combustion engine; EW, ethanol–water mixture; EWAG, ethanol–water–acetic acid–glycerol mixture; EtOH, ethanol; GlyOH, glycerol; AcAc, acetic acid; Y_{H₂}, hydrogen yield; GHSV, gas hourly space velocity; GC, gas-chromatograph.

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the unpurified or crude ethanol from fermentation broth could be used directly in steam reforming reaction to produce hydrogen rich-stream, which can be more energy efficient and cost effective for commercial applications [5–7]. The crude or raw bio-ethanol contains various impurities, mainly higher alcohols, with minor acids, aldehydes, ethers, esters, etc. These impurities and ethanol concentration may vary based on the type of biomass raw materials exploited. The concentration of ethanol from fiber beer is around 5–6% with water and other residues [6–8] as well as the raw bio-ethanol obtained from sugar beet contains 87% impurities and also higher alcohols like methyl-3-butan-1-ol, etc. [8–10]. In the present study, a simulated bio-ethanol mixture coming from waste by-product of cheese industry was considered, taking into account that the most common impurities from the fermentation broth of cheese by-products are acetic acid, glycerol and other minor impurities [6].

1.1. Catalytic membrane reactor

Applying process intensification strategy to hydrogen production via BESR reaction can be a huge advantage both from an environmental and economical point of view and, in this contest, membrane reactor technology could represent the tool to achieve this intent. Indeed, the MR makes possible the integration of two unit operations, i.e. reaction and hydrogen separation process, in only one unit, representing an economical benefit with respect to the conventional systems as well as avoiding the utilization of further hydrogen separation devices [11]. In the meanwhile, MR could be used for CO₂ sequestration during BESR process [12]. However, the synergic effect of catalyst and membrane has been poorly investigated in SR of ethanol carried out in MRs. As well known in literature, both catalyst and membrane play an important role to achieve high MR performances in terms of ethanol conversion and hydrogen yield and their joint effect should be deeply studied in order to achieve maximum MR efficiency and performance.

The MR technology applied to SR of ethanol is reported in several scientific articles and literatures [13–19] and, in the majority of them, the benefits due to the MRs use for producing high purity hydrogen over the conventional systems is described and emphasized.

As recently reported by Iulianelli and Basile [16], when a dense self-supported Pd–Ag membrane is used in a MR, exhibiting full hydrogen perm-selectivity with respect to the other gases, poor hydrogen permeability is observed, making the process less economical viable for industrial applications. In other aspects, composite porous supported membranes like ceramic or alumina based Pd-MRs provide not full hydrogen perm-selectivity, but higher hydrogen fluxes compared to dense. Furthermore, to limit the cost of Pd-based membranes, Pd thickness is reduced, proportionally increasing the hydrogen flux permeating through the membrane. Composite Pd-based membranes have been already explored in many applications and, as a particular case, also in SR reactions to produce hydrogen via ethanol steam reforming reaction, showing relatively high hydrogen perm-selectivity compared to other gases [17,19–23,25,28]. Composite Pd supported on porous stainless steel (Pd/PSS) MRs provide both factors, i.e. reasonable perm-selectivity with high hydrogen permeability and also economical benefits. Moreover, porous substrate provides good mechanical stability, resistance to cracking and simplicity in module construction [20]. Therefore, the aim of this work is to explore both the potentiality of a composite Pd supported porous stainless steel MR in BESR and the effects of crude bio-ethanol impurities like acetic acid and glycerol on MR performances in terms of bio-ethanol conversion, hydrogen recovery factor (HRF), hydrogen permeate purity (HPP), hydrogen yield and selectivity of product gases. Moreover, a comparison of two commercial catalysts and their behavior in MR is also reported.

Table 1

Composition of the simulated mixture in steam reforming of bio-ethanol.

| Components of bio-ethanol mixture | Composition (vol.%) |
|--|---------------------|
| H ₂ O | 76 |
| C ₂ H ₅ OH | 19 |
| C ₃ H ₈ O ₃ | 4 |
| C ₂ H ₃ OOH | 1 |

2. Methods and materials

2.1. Experimental set-up

The MR experimental set-up is shown in Fig. 1. It consists of mass flow controllers (Brooks Instruments 5850S), temperature controllers and a membrane reactor module housing a composite porous stainless steel supported Pd membrane. The catalyst is packed inside the MR annulus. The reaction pressure is controlled by means of a back pressure controller at the retentate side. Two different mixtures (ranging from 0.05 to 0.2 mL/min as a mass flow rate) are supplied by using a HPLC pump (furnished by Dionex) to a pre-heating zone and, then, to the MR. The first one is a simulated bio-ethanol mixture containing some typical by-products as impurities, Table 1, while the second one is the first mixture without the impurities, useful for analyzing the effects of the presence of the by-products. Both mixtures are pre-heated before entering in the MR, where the reaction temperature is kept constant at 400 °C. No sweep gas is used in the MR permeate side, which is maintained constant at 1.0 bar (absolute) in the whole experimental campaign. The products from retentate side are passed over a cold trap in order to condense the unreacted (condensable) products. Both permeate and retentate dry stream compositions are analyzed by a temperature programmed HP 6890 gas chromatograph (GC) with two thermal conductivity detectors at 250 °C and argon used as a carrier gas. GC is equipped with three packed columns: Porapak R 50/80 (8 ft × 1/8 in.) and CarboxenTM 1000 (15 ft × 1/8 in.) connected in series, and a Molecular Sieve 5 Å (6 ft × 1/8 in.).

2.2. Composite Pd/PSS membrane reactor

The MR consists of a tubular stainless steel module with length 280 mm, internal diameter of 20 mm, housing a PSS supported Pd tubular membrane having 20 μm thickness of Pd layer, 7 cm of active layer length on the porous support and an outer diameter around 1 cm, Fig. 1. The Pd-based membrane was produced by electroless plating using a stainless steel tubular macroporous support as reported in [22]. The porous support was welded to two non-porous AISI 316L tubes, one of them closed in order to provide proper housing inside the reactor.

2.3. Reaction test procedure

In this study, two commercial non-noble catalysts Ni/ZrO₂ (CAT-ACOL) and Co/Al₂O₃ (Johnson Matthey) were used, respectively, in BESR. In both cases, 3.0 g of catalyst in pellet shape were packed with glass spheres (2 mm diameter) in the MR annulus. Furthermore, the wt.% in dry conditions of Co metal is equal to 15% and 25% for Ni. The tubular reactor module with catalyst bed was heated up to 400 °C under N₂ flow with slow heating rate. Before reaction test, the catalyst was subjected to reduction for 2 h under H₂ flow at 400 °C (under atmospheric pressure). After reduction step, reaction tests were conducted in the MR shell side and each experimental result represents an average value taken, at least, within three experimental reaction cycles realized during 90–120 min of testing at steady state conditions. The thermocouple was inserted in the shell side, separated from the reaction side. The experimental

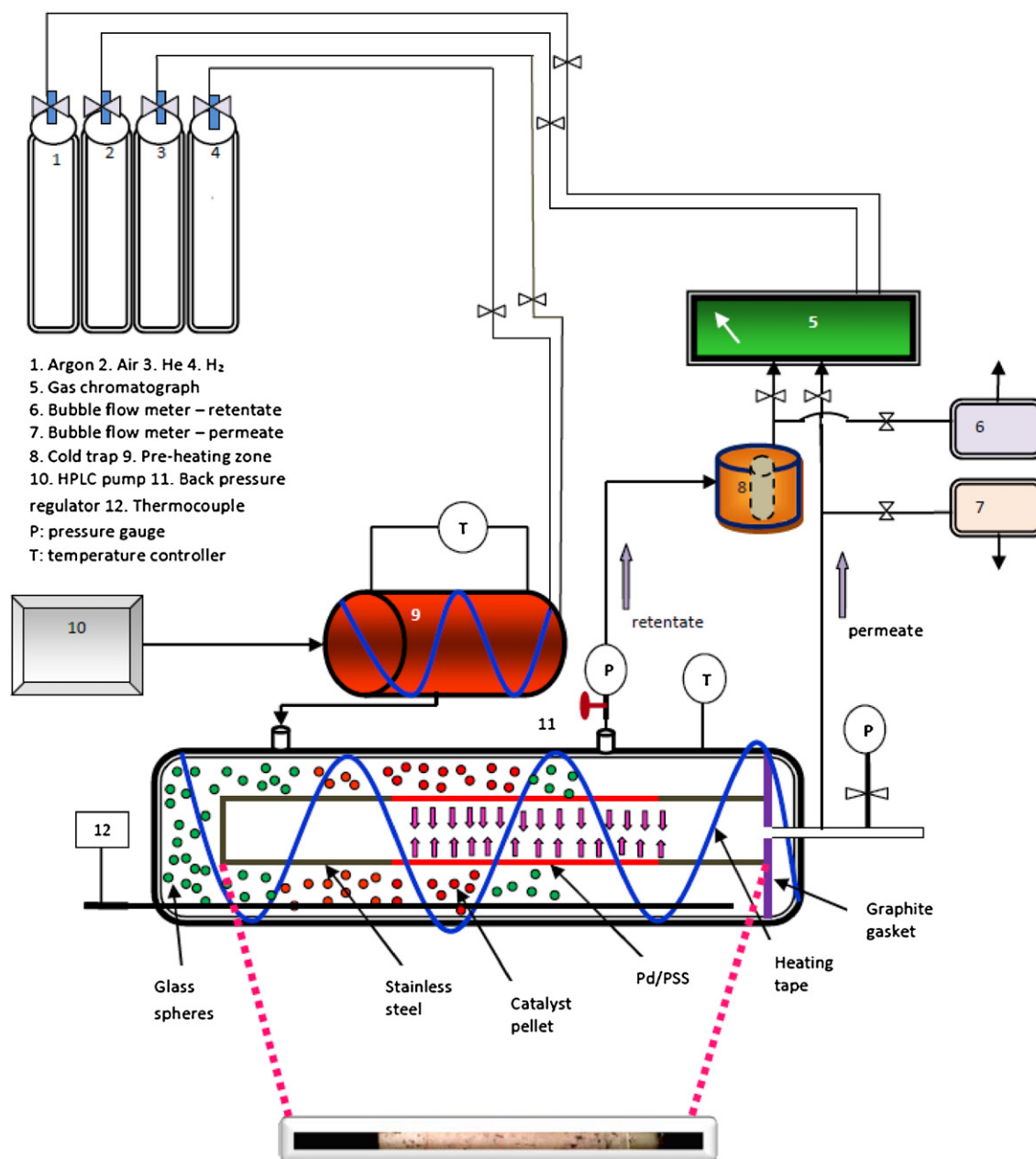


Fig. 1. Membrane reactor experimental set-up.

tests were performed in a MR configuration, where one side is closed and the reformed gases in permeate and retentate sides were analyzed by GC. Membrane reactor performances were evaluated in terms of the following Eqs. (2)–(5):

$$\text{Conversion(into gas)} = \frac{\text{CO}_{2,p,r} + \text{CH}_{4,p,r} + \text{CO}_{p,r}}{2\text{EtOH}_{in} + 3\text{GlyOH}_{in} + 2\text{AcAc}_{in}} \quad (2)$$

where $\text{CO}_{p,r}$, $\text{CO}_{2,p,r}$, $\text{CH}_{4,p,r}$ represent the outlet molar flow rates in both permeate and retentate sides of carbon monoxide, carbon dioxide and methane produced during the reaction; EtOH_{in} , GlyOH_{in} and AcAc_{in} represent the inlet molar flow rate of ethanol, glycerol and acetic acid (the two last ones, if any).

$$\text{Hydrogen recovery factor(HRF)} = \frac{\text{H}_{2,p}}{\text{H}_{2-\text{TOT}}} \cdot 100 \quad (3)$$

where $\text{H}_{2,p}$ is the hydrogen molar flow rate collected in the permeate side and $\text{H}_{2-\text{TOT}}$ is the total hydrogen molar flow rate produced

during the reaction.

$$\text{Hydrogen permeate purity(HPP)} = \frac{\text{H}_{2,p}}{\text{H}_{2,p} + \text{CO}_p + \text{CO}_{2,p} + \text{CH}_{4,p}} \cdot 100 \quad (4)$$

where $\text{H}_{2,p}$, CO_p , $\text{CO}_{2,p}$, $\text{CH}_{4,p}$ are, respectively, the hydrogen, carbon monoxide, carbon dioxide and methane molar flow rates collected in the permeate side.

$$\text{Hydrogen yield}(Y_{\text{H}_2}) = \frac{\text{H}_{2-\text{produced}}}{6\text{EtOH}_{in} + 7\text{GlyOH}_{in} + 4\text{AcAc}_{in}} \cdot 100 \quad (5)$$

where $\text{H}_{2-\text{produced}}$ represents the total hydrogen molar flow rate produced during BESR and 6EtOH_{in} , 7GlyOH_{in} and 4AcAc_{in} the maximum hydrogen theoretically producible, when the simulated bio-ethanol mixture consisting of acetic acid and glycerol beside ethanol and water with $\text{EtOH}:\text{H}_2\text{O}:\text{GlyOH}:\text{AcAc} = 1:13:0.18:0.04$

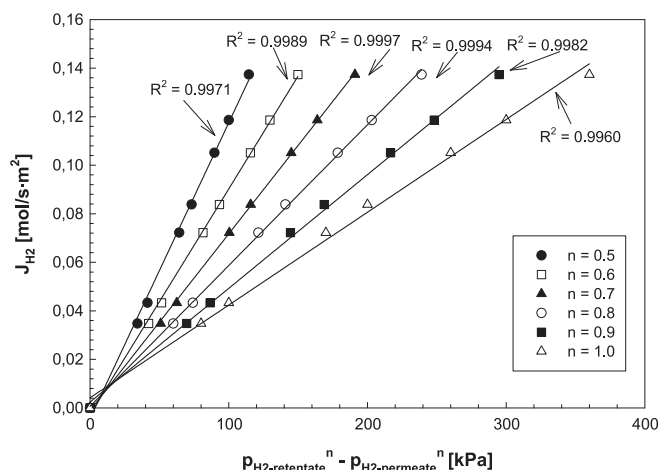


Fig. 2. H₂ permeating flux through the Pd/PSS membrane at 400 °C vs. H₂ permeation driving force at different “n” factor.

molar ratio (denoted as EWAG mixture), is supplied to the MR. In case of the ethanol/water mixture with EtOH:H₂O = 1:13 (denoted as EW), the contribute related to GlyOH and AcAc is not considered.

$$\text{Selectivity}_i(S_i) = \frac{Q_{i-\text{TOT}}}{Q_{\text{H}_2-\text{TOT}} + Q_{\text{CO}_2-\text{TOT}} + Q_{\text{CO}-\text{TOT}} + Q_{\text{CH}_4-\text{TOT}}} \cdot 100 \quad (6)$$

Selectivity of the gases coming out from the MR, where $i = \text{H}_2, \text{CO}, \text{CO}_2, \text{CH}_4$ and $Q_{i-\text{TOT}}$ represents the total molar flow rate of the i -compound; $Q_{\text{H}_2-\text{TOT}}, Q_{\text{CO}-\text{TOT}}, Q_{\text{CH}_4-\text{TOT}}, Q_{\text{CO}_2-\text{TOT}}$ represent the total molar flow rate of hydrogen, carbon monoxide, methane and carbon dioxide, respectively, coming out from the MR.

3. Results and discussions

3.1. H₂ permeation test

Permeation tests are an important step to verify the H₂ flux permeating through the membrane and its selectivity toward the other gases of interest as well as to evaluate the membrane permeation characteristics after reaction tests. Firstly, permeation tests were performed flowing pure hydrogen through the Pd/PSS membrane at 400 °C with a transmembrane pressure difference depending on the variation of the retentate pressure in the range of 2–4 bar and keeping constant permeate pressure at 1.0 bar.

Generally, the hydrogen permeation through a Pd-based membrane is described by the following Eq. (7):

$$J_{\text{H}_2} = \text{Pe}(p_{\text{H}_2,r}^n - p_{\text{H}_2,p}^n) \quad (7)$$

where J_{H_2} = hydrogen flux permeating through Pd/PSS membrane; $\text{Pe} = \text{H}_2$ permeance; $p_{\text{H}_2,r}^n$ and $p_{\text{H}_2,p}^n$ = hydrogen partial pressures in the retentate and permeate sides, respectively.

The dependence factor “n” for the hydrogen partial pressure ranges between 0.5 and 1.0 and is used as an indicator for the rate-controlling step of hydrogen permeation. As shown in Fig. 2, in the present study, the factor $n = 0.7$ is evaluated to be the most accurate compared to the other ones owing to the highest linear regression correlation coefficient equal to $R^2 = 0.9997$.

Furthermore, after each reaction test, a hydrogen permeation test was performed to verify the eventual variation of the membrane permeation characteristics. In particular, Fig. 3 shows the hydrogen flux before and after a reaction test as well as after a regeneration step (realized as a hydrogen treatment via permeation through the membrane) performed as a pure hydrogen stream (around 18 mL/min) flowed in the reaction side for 1 h at 400 °C. In particular, Fig. 3 shows that after 1 h of regeneration procedure,

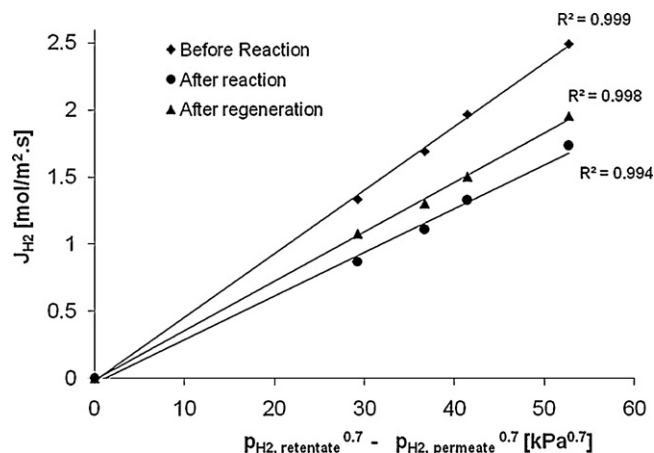


Fig. 3. Hydrogen flux vs. driving force – hydrogen partial pressure difference at retentate and permeate to the power of 0.7.

the hydrogen permeation characteristics are not completely recovered. Then, each regeneration step was performed for, at least, 2 h up to recover completely the hydrogen permeation behavior of the Pd composite membrane.

3.2. Effect of reaction pressure

As above mentioned, the steam reforming of EW and EWAG were tested to study the effect of bio-ethanol impurities in BESR performed in a Pd/PSS MR. Firstly, the mixtures (0.2 mL/min feed flow rate) were tested over Ni/ZrO₂ catalyst at 400 °C, GHSV equal to 3200 h^{−1} (STP) and in a reaction pressure range of 8–12 bar. From Fig. 4, both bio-ethanol conversion and HRF increase as the reaction pressure increases. As a general consideration, a reaction pressure increase has two main effects on the MR system. Indeed, from a thermodynamic point of view at higher pressures bio-ethanol conversion is lowered since BESR proceeds toward the products with an increase of the moles number. The same scenario takes place also in the presence of impurities such as glycerol and acetic acid, because steam reforming of glycerol (8) and acetic acid (9) both proceed with an increase of moles number toward the products.

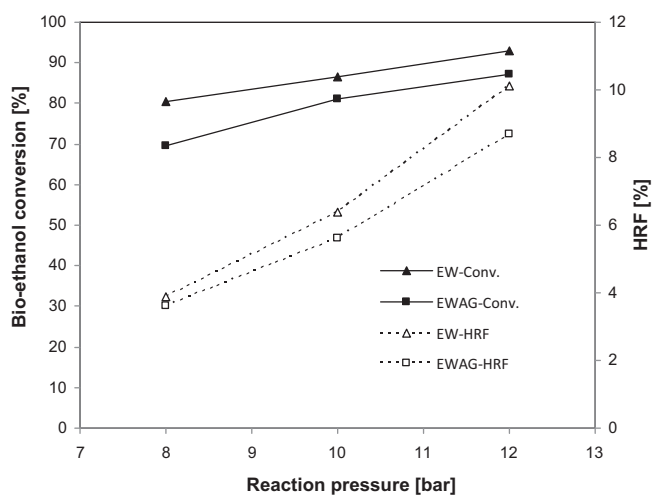
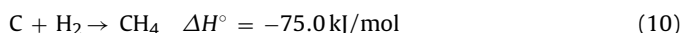


Fig. 4. Bio-ethanol conversion and HRF against the reaction pressure in Pd/PSS MR over Ni/ZrO₂ catalyst at 400 °C, SR of EW and EWAG mixtures (bio-ethanol conversion as solid lines and HRF as dotted lines).

Otherwise, the higher the reaction pressure the higher the hydrogen permeation driving force, which allows a higher hydrogen stream to be removed from the reaction side and collected in the permeate side, causing a shift effect of the BESR reaction (and, in case, also of both glycerol and acetic acid steam reforming) toward the products. As illustrated in Fig. 4, it is evident that the benefit due to the pressure increase (the shift effect) is more pronounced and prevalent than the detrimental effect caused by the thermodynamic, globally determining an increasing trend of conversion with the pressure.

As previously mentioned, higher reaction pressures involve higher hydrogen permeation driving force, which determines higher hydrogen flux permeating through the membrane. Then, HRF increases with reaction pressure. However, HRF values are quite low owing to carbon deposition on the membrane surface, which affects negatively the hydrogen permeation through the Pd/PSS membrane. Indeed, as an indirect proof of coke presence on the membrane surface, during the regeneration step in which pure hydrogen is flowed in the MR, methane formation was detected as the reaction (10) reported below:



No oxygen was used to regenerate the catalyst and eliminate the coke deposits on the membrane surface because, firstly, higher temperature are required ($\sim 600^\circ\text{C}$) and, secondly, to avoid the formation of palladium oxides, which could damage dramatically the Pd-layer and its performances. However, when nickel catalyst is used, carbon formation during reaction is high, causing catalyst deactivation and, also, inhibition of hydrogen permeation through membrane surface. Furthermore, by performing BESR with the EW mixture, higher HRF and conversion are obtained compared to the EWAG mixture, Fig. 4. This is due to the fact that the presence of glycerol and acetic acid affect negatively the reaction system because more coke is produced, further depressing the MR performances. This is also confirmed by Le Valant et al. [8–10], who reported that, by adding acid or alcohol impurities to a pure ethanol–water mixture, bio-ethanol conversion, hydrogen selectivity and catalyst stability are lowered. In particular, coke can be formed owing to dehydration reaction of glycerol to ethylene and/or propylene, which are precursors of coke formation [24]. However, to avoid or deplete coke formation, Adihikari et al. [29] reported that temperature higher than around 550°C could depress the formation of coke. Unfortunately, in our work the PSS supported Pd-membrane cannot be used at $T > 400^\circ\text{C}$ and, then, this solution cannot be proposed.

3.2.1. Comparison of two catalysts in MR: Ni/ZrO₂ vs. Co/Al₂O₃

BESR using only the EWAG mixture with the composition of Table 1 was also performed in the Pd/PSS MR packed with Co–Al₂O₃ catalyst. Fig. 5 shows that, as previously explained, also for Co-based catalyst both bio-ethanol conversion and HRF increase with reaction pressure. The conversion values achieved in the MR over Co-based catalyst range between 42% and 82%, respectively, at 8.0 and 12.0 bar, while over Ni-based catalyst they vary from 70% at 8.0 bar to 87% at 12.0 bar. Therefore, it can be concluded that nickel is more active in bio-ethanol conversion compared to cobalt. Nevertheless, even though nickel better performs in terms of conversion than cobalt, when it is used during BESR reaction, lower HRFs are reached. This depends on the characteristics of the Co-based catalyst, which is more selective than Ni-based catalyst in the production of hydrogen, as reported as a higher hydrogen selectivity in Table 2. More in detail, Co is less active in the dehydrogenation reaction of ethanol to acetaldehyde, which – when decomposed – gives rise to the formation of methane, by favoring indirectly higher hydrogen formation instead of methane. Indeed, hydrogen selectivity (6) over cobalt ranges from $\sim 54\%$ at 8.0 bar to $\sim 49\%$ at 12.0 bar,

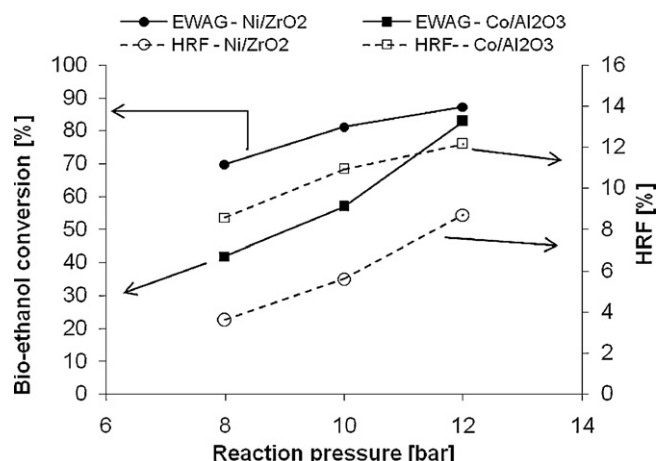


Fig. 5. Bio-ethanol conversion and HRF against the reaction pressure in PSS/Pd MR over Ni and Co catalysts at 400°C .

Table 2

Selectivity of product gases at different reaction pressures during BESR reaction performed in a Pd/PSS MR at 400°C over Ni/ZrO₂ and Co/Al₂O₃ catalysts.

| P (bar) | S _{H₂} | S _{CO} | S _{CH₄} | S _{CO₂} |
|--------------------------------------|----------------------------|-----------------|-----------------------------|-----------------------------|
| a. Ni/ZrO ₂ | | | | |
| 8 | 36.0 | 3.2 | 23.2 | 37.6 |
| 10 | 33.1 | 2.3 | 27.1 | 37.4 |
| 12 | 31.2 | 1.2 | 28.4 | 39.2 |
| b. Co/Al ₂ O ₃ | | | | |
| 8 | 53.7 | 3.5 | 8.0 | 34.8 |
| 10 | 49.6 | 2.7 | 11.1 | 36.6 |
| 12 | 48.5 | 3.1 | 11.9 | 36.5 |

while over nickel it ranges from $\sim 36\%$ at 8.0 bar to 31% at ~ 12.0 bar. As a consequence, also the hydrogen yield results to be higher when using the Co-based catalyst than the Ni-based one, Fig. 6.

During the regeneration step, carbon deposition was confirmed by GC analysis using both the catalysts. In the case of Ni, carbon deposition is more pronounced, probably because carbon coke is less reactive [26]. Moreover, ZrO₂ as a support is not particularly active in steam reforming reaction compared to alumina. As a consequence, the coke formation takes place with higher deposition rates, showing low reactive coke during regeneration compared to the other catalyst support materials like alumina [26].

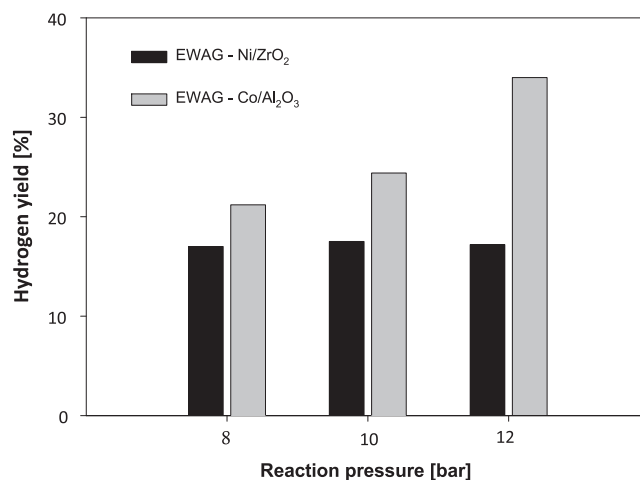


Fig. 6. Hydrogen yield against reaction pressure at 400°C over Ni/ZrO₂ and Co/Al₂O₃ catalysts in Pd/PSS MR.

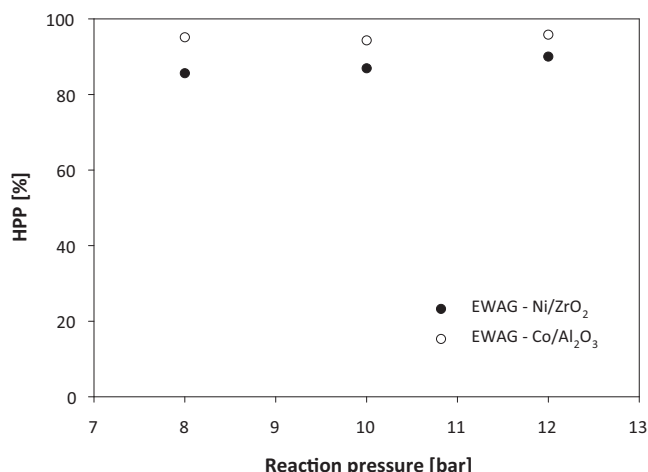
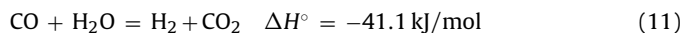


Fig. 7. Hydrogen permeate purity against reaction pressure at 400 °C over Ni–ZrO₂ and Co–Al₂O₃ catalysts in Pd/PSS MR.

Concerning the hydrogen permeate purity, Fig. 7 illustrates that HPP does not vary with pressure in both catalysts used. In detail, depending on the greater hydrogen production when Co-based catalyst is packed in the Pd/PSS MR, HPP is higher compared to the Ni-based one. Indeed, in the case of Co catalyst, both hydrogen yield, Fig. 6, and hydrogen selectivity, Table 2, are higher, globally favoring a higher hydrogen content to be collected in the permeate side. Therefore, in this case, HPP is around 95%, while in the case of Ni catalyst it is around 85%, Fig. 7.

Table 2 summarizes the product gases selectivity at different reaction pressures obtained during BESR in the Pd/PSS MR using the simulated EWAG mixture and over both Ni and Co-based catalysts, respectively. The hydrogen selectivity over cobalt is higher compared to nickel in the pressure range of 8.0–12.0 bar, pointing out that Co–Al₂O₃ catalyst is more appropriate to be used in BESR reaction. Furthermore, CO selectivity decreases by increasing the reaction pressure, confirming the membrane effect, which gives a positive influence on CO reduction by shifting the water gas shift reaction (11) to consume more CO.



This trend can be justified by considering the correspondent increasing trend of CO₂ selectivity with reaction pressure, Table 2. However, in the case of Ni–ZrO₂ catalyst, hydrogen is consumed in methanation reaction and, as a consequence, the hydrogen selectivity is lower. This is also confirmed by Seelam et al. [27], who demonstrated in a conventional system that Ni-based catalyst is more prone to methane formation by methanation reaction at low temperatures (i.e. <400 °C).

3.3. Effect of GHSV over cobalt catalyst in MR

As a further investigation of this work, the influence of GHSV variation on BESR reaction (using only the simulated EWAG mixture) performed in the Pd/PSS MR packed with only Co–Al₂O₃ catalyst was studied. As expected, a rapid increase of bio-ethanol conversion and HRF with a decrease of the GHSV from 3200 to 800 h^{−1} was found at 12 bar, Fig. 8. By decreasing the space velocity, a higher residence or contact time between the catalyst and reactants is favored. Thus, this is more effective for higher hydrogen production and, then, for higher hydrogen yield, Fig. 8. At GHSV=800 h^{−1}, the HRF is enhanced up to 40% with respect to 12% at GHSV=3200 h^{−1}. In the meanwhile, also the bio-ethanol conversion increases from 83% (at 3200 h^{−1}) to 94% (at 800 h^{−1}). From Fig. 8, it can be concluded that the hydrogen yield increases

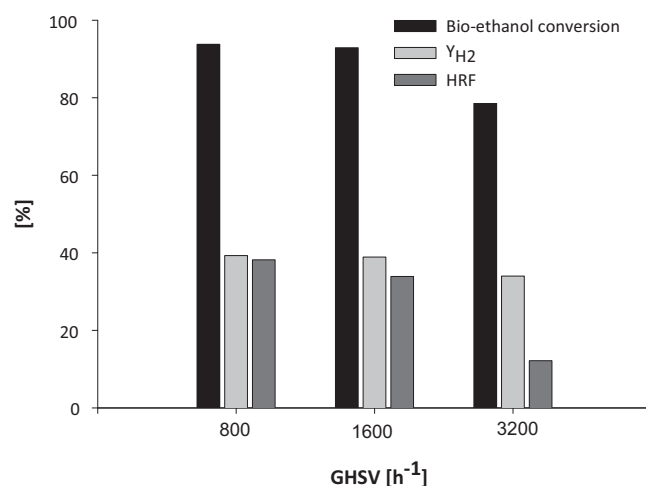


Fig. 8. Bio-ethanol conversion, hydrogen yield (Y_{H2}) and HRF against reaction pressure at 400 °C over Co/Al₂O₃ catalysts for SR of EWAG mix in Pd/PSS MR.

Table 3

Molar composition and molar flow rate of the gaseous products obtained by SR of EWAG mix in a Pd/PSS MR for both permeate and retentate streams without vapors cooled down before GC analysis. Operating conditions: *P* = 12 bar, *T* = 400 °C, GHSV = 800 h^{−1} over Co/Al₂O₃ catalysts.

| | Retentate | | Permeate | |
|-----------------|-----------------------|---------------------------|-----------------------|---------------------------|
| | Molar composition [%] | Molar flow rate [mol/min] | Molar composition [%] | Molar flow rate [mol/min] |
| H ₂ | 37.8 | 2.324E−04 | 94.52 | 1.44E−04 |
| CO | 1.6 | 9.96E−06 | 0.14 | 2.13E−07 |
| CH ₄ | 13.0 | 8.02E−05 | 0.65 | 9.86E−07 |
| CO ₂ | 47.6 | 2.93E−04 | 4.70 | 7.16E−06 |

by decreasing the GHSV. In fact, lowering the GHSV is advantageous for generating more hydrogen in the reaction side, resulting in a higher retentate hydrogen partial pressure that enhances the hydrogen permeation driving force with a consequent more effective shifting of BESR reaction toward the products. Therefore, this gives more bio-ethanol consumption and a greater hydrogen production as well as a higher hydrogen stream permeating through the membrane. However, in all the experimental values reported in Fig. 8, the HPP was almost constant around 95% and, to better clarify this point, Table 3 shows the permeate and retentate molar composition as well as the molar flow rate of the gaseous products in both permeate and retentate streams (without vapors, cooled down before GC analysis) at *P* = 12 bar, *T* = 400 °C and GHSV = 80 h^{−1}.

4. Conclusions

Bio-ethanol steam reforming reaction was carried out in a Pd/PSS MR packed, respectively, with two different commercial reforming catalysts, i.e. Ni–ZrO₂ and Co–Al₂O₃. The reaction was performed at 400 °C from 8.0 to 12.0 bar as a reaction pressure keeping constant the permeate pressure at 1.0 bar. Two simulated bio-ethanol mixtures were when supplied to the MR, by comparing the effect of the presence of such impurities as glycerol and acetic acid over a simple ethanol/water mixture. The simulated bio-ethanol mixture containing impurities was related to a typical bio-ethanol mixture produced from fermentation of cheese. The effect of reaction pressure and GHSV on the MR performance was evaluated in terms of bio-ethanol conversion, HRF, HPP and hydrogen yield and product gases selectivity. The permeating flux of H₂ through the membrane was declining after each reaction test, thus resulting in decreasing in the overall efficiency of MR due to

coke deposition on the membrane surface, causing a decrease of the MR performances, particularly the HRF. The impurities are, also, major precursors for the carbon coke formation, which was confirmed during the GC analysis of regeneration process performed by flowing pure hydrogen in the reaction side.

Concerning BESR performed in the Pd/PSS MR by supplying the EWAG mixture, the use of the Co-based catalyst at 12.0 bar of reaction pressure performs better in terms of HRF (nearly 40%), HPP (95%) and hydrogen yield of 40% than Ni-based one, probably because Ni is more prone to produce methane than hydrogen, globally lowering the hydrogen produced in the reaction side. On the contrary, using the latter, higher conversions than the Co-based one are achieved. However, with the aim of producing as much high purity hydrogen as possible, the best results of this work can be identified with the Pd/PSS MR packed with the Co-Al₂O₃ catalyst and working at 12.0 bar of reaction pressure, where 94% of bio-ethanol conversion, HRF around 40% with a HPP of 95% and a hydrogen yield of around 40% were reached. In the future, as a next step of investigation, a real bio-ethanol mixture (containing also other minor by-products) will be supplied to the Pd/PSS MR in a steam reforming process to compare the experimental performances achieved using the simulated EWAG mixture.

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